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(54) A method for forming a thin film

(57) A reactive solution with an amount of 250 mL is made of distilled water and $LiOH \cdot H_2O$ (4M) melted in the distilled water. Then, the reactive solution is put in a flow-type reactor, and is flown in between an anode electrode and a cathode electrode set in the flow-type reactor at a given temperature and a given flow rate. Then, a given voltage is applied between the anode electrode and the cathode electrode with dropping an oxidizer of hydrogen peroxide (H_2O_2) into the reactive solution to form a lithium-cobalt oxide thin film on the anode electrode.

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Description

Background of the Invention

1. Field of the Invention

[0001] This invention relates to a method for forming a thin film, particularly to a method for forming a thin film suitable for a secondary battery field usable for mobile electronic device and electric automobiles.

2. Related Art Statement

[0002] So far, a sol-gel method, a CVD method or a PVD method is employed as a thin film-forming method. These methods require multistage process including a heating process, a high vacuum condition, or a high energy condition accompanied with a substrate-heating process or a plasma-generating process. Therefore, those methods require large scale and complicate apparatus, resulting in large cost and complicate operationality in use.

[0003] Moreover, the above high energy condition runs counter to global environmental protection, resource saving and energy saving. Therefore, a new thin film-forming method without the above high energy condition has been desired.

Summery of the Invention

[0004] It is an object of the present invention to provide a new thin film-forming method not including a high energy condition due to firing, heating or plasma generation.

[0005] This invention relates to a method for forming a thin film (hereinafter, often called as a "first thin film-forming method) comprising the steps of:

setting an anode electrode and a cathode electrode in a reactive solution,
flowing the reactive solution in between the anode electrode and the cathode electrode at a given flow rate, and
applying a given voltage between the anode electrode and the cathode electrode, thereby to synthesize a compound thin film including the components of the reactive solution and the anode electrode on the anode electrode.

[0006] This invention also relates to a method for forming a thin film (hereinafter, often called as a "second thin film-forming method) comprising the steps of:

setting an anode electrode and a cathode electrode in a reactive solution,
flowing the reactive solution in between the anode electrode and the cathode electrode at a given flow rate, and
applying a given voltage between the anode electrode and the cathode electrode, thereby to synthesize a compound thin film including the components of the reactive solution and the anode electrode on a given substrate arranged in the flow direction of the reactive solution.

[0007] The inventors related to the present invention have been intensely studied for developing a new thin film-forming method not including a high energy process. As a result, they have found out surprisingly that when a reactive solution incorporating a component of a desired thin film is flown in between an anode electrode and a cathode electrode to which a given voltage is applied, the desired compound thin film including the component of the reactive solution and another component of the anode electrode is synthesized directly on the anode electrode. Then, they have also found out that when the anode electrode and the cathode electrode are set in a static reactive solution and a given voltage is applied between the anode electrode and the cathode electrode, the compound thin film is not synthesized on the anode electrode.

[0008] The first thin film-forming method of the present invention is made on the discovery of the above phenomenon. The first thin film-forming method enables the desired compound thin film to be formed directly on the anode electrode without the high energy condition including the substrate-heating process and the plasma generation.

[0009] Moreover, the inventors have found out that if the flow rate of the reactive solution and the voltage applied between the anode electrode and the cathode electrode are controlled appropriately, the compound thin film composed of the components of the reactive solution and the anode electrode can be synthesized on a given substrate which is arranged in the flow direction of the reactive solution.

[0010] The cause of the thin film formation on the given substrate may be considered as follows: That is, the reactive solution erodes and melts the superficial parts of the anode electrode, and thus, the melted anode electrode material and the reactive solution arrive at and synthesized on the substrate.

[0011] The second thin film-forming method of the present invention is made on the discovery of the above phenomenon. The second thin film-forming method enables the compound thin film to be formed on the given substrate without the high energy condition including the substrate-heating process and the plasma generation.

Brief Description of the Drawings

[0012] The invention will be more particularly described with reference to the accompanying drawings:

Fig. 1 is a graph showing a X-ray diffraction spectrum of a lithium-cobalt oxide thin film synthesized by the thin film-forming method of the present invention.

Description of the Preferred Embodiments

[0013] The invention will be described in detail as follows.

[0014] In the first thin film-forming method of the present invention, the flow rate of the reactive solution is not restricted even if the compound thin film, composed of the components of the reactive solution and the anode electrode, can be synthesized on the anode electrode. The flow rate of the reactive solution is determined on the kind of the reactive solution, the anode electrode material, the kind of the compound thin film to be formed and the forming speed of the compound thin film.

[0015] However, it is preferable that the upper limit value of the flow rate of the reactive solution is 100 mL/minute, particularly 20 mL/minute. Moreover, it is preferable that the lower limit value of the flow rate of the reactive solution is 1 mL/minute, particularly 5 mL/minute. Thereby, irrespective of the kinds of the reactive solution and the anode electrode material or the like, the compound thin film can be formed on the anode electrode uniformly.

[0016] The voltage to be applied between the anode electrode and the cathode electrode is not restricted even if the compound thin film is formed on the anode electrode according to the present invention. However, it is preferable that the voltage is applied so that a current with a range of 0.01-5 mA/cm^3 is flown between the anode electrode and the cathode electrode. Thereby, the compound thin film can be formed uniformly with the enhancement of the thin film-forming speed.

[0017] In the second thin film-forming method of the present invention, the flow rate of the reactive solution is not limited even if the compound thin film, composed of the components of the reactive solution and the anode electrode, can be formed on the given substrate.

[0018] However, it is desired that the upper limit value of the flow rate of the reactive solution is 200 mL/minute, particularly 50 mL/minute. Moreover, it is desired that the lower limit value of the flow rate of the reactive solution is 2 mL/minute, particularly 5 mL/minute. Thereby, the reactive solution can erode the superficial parts of the anode electrode effectively, and transport the thus melted anode electrode material to on the given substrate. Moreover, the compound thin film can be synthesized uniformly on the given substrate irrespective of the kind of the reactive solution or the like.

[0019] As mentioned in the first thin film-forming method, it is desired that the voltage is applied between the anode electrode and the cathode electrode so that a current with a range of 1-5 mA/cm^3 is flown therebetween. The reactive solution is selected on the kind of the compound thin film to be formed.

[0020] In the second thin film-forming method of the present invention, the cathode electrode and the anode electrode may be made of a well known electrode material. Moreover, the substrate may be made of any material in any shape, depending on the use of the compound thin film.

[0021] Moreover, in the first thin film-forming method of the present invention, the cathode electrode may be made of a well known electrode material, and the anode electrode may be made of a given material depending on the kind of the compound thin film. For example, in formation of a lithium-cobalt thin film, a cobalt electrode may be used as the anode electrode.

[0022] If an oxide thin film is formed on the anode electrode according to the thin film-forming method of the present invention, it is desired to incorporate an oxidizer in the reactive solution. Thereby, the components of the reactive solution and the anode electrode can be easily oxidized, the oxide thin film can be formed on the anode electrode or the substrate uniformly in a short time.

[0023] Hydrogen peroxide (H_2O_2) and $Na_2S_2O_3$ may be exemplified as the oxidizer. Particularly, in the formation of the lithium-cobalt thin film, the hydrogen peroxide is preferably used.

Examples:

[0024] This invention will be concretely described with reference to the following examples.

[0025] First of all, a cobalt electrode as the anode electrode and a platinum electrode as the cathode electrode were set in a flow-type reactor.

[0026] Then, a reactive solution with an amount of 250 mL was made of distilled water and LiOH H_2O (4M) melted in the distilled water. The reactive solution was put in the flow-type reactor, and then, held at 150°C and flown in between the cobalt electrode and the platinum electrode at a flow rate of 5 mL/minute.

[0027] Then, a given voltage was applied between the electrodes so that a current density of 1 mA/cm^3 was flown therebetween, and hydrogen peroxide (H_2O_2) was dropped off into the reactive solution at a rate of 1 mL/minute.

[0028] Three hours later, the cobalt electrode was taken out of the flow-type reactor, and the surface of the cobalt electrode was analyzed by X-ray diffraction. The thus obtained X-ray diffraction pattern was shown in Fig. 1.

[0029] As is apparent from Fig. 1, diffraction peaks from hexagonal $LiCoO_2$ (R3m) are observed on the surface of the cobalt electrode. That is, it is turned out that a compound thin film made of $LiCoO_2$ crystal is formed on the cobalt electrode as the anode electrode.

[0030] Moreover, it is turned out that from SEM observation, the compound thin film has a layered structure.

[0031] Although this invention bas been described in detail with reference to the above examples, this invention is not limited to the above disclosure and every kind of variation and modification may be made without departing from the scope of the present invention.

[0032] According to the present invention, a com-

pound thin film can be directly synthesized on an anode electrode or a given substrate at room temperature. Therefore, a high energy condition including a high temperature substrate heating process, a plasma generation or the like is not required, different from a conventional CVD method and PVD method. As a result, a new thin film-forming method not including the high energy condition can be provided.

Claims

1. A method for forming a thin film comprising the steps of:

   setting an anode electrode and a cathode electrode in a reactive solution,
   flowing the reactive solution in between the anode electrode and the cathode electrode at a given flow rate, and
   applying a given voltage between the anode electrode and the cathode electrode, thereby to synthesize a compound thin film including the components of the reactive solution and the anode electrode on the anode electrode.

2. A method for forming a thin film as defined in claim 1, wherein the flow rate of the reactive solution is set within 1-100 mL/minute.

3. A method for forming a thin film as defined in claim 1 or 2, further comprising the step of incorporating oxidizer in the reactive solution, whereby an oxide thin film including the components of the reactive solution and the anode electrode is formed on the anode electrode.

4. A method for forming a thin film comprising the steps of:

   setting an anode electrode and a cathode electrode in a reactive solution,
   flowing the reactive solution in between the anode electrode and the cathode electrode at a given flow rate, and
   applying a given voltage between the anode electrode and the cathode electrode, thereby to synthesize a compound thin film including the components of the reactive solution and the anode electrode on a given substrate arranged in the flow direction of the reactive solution.

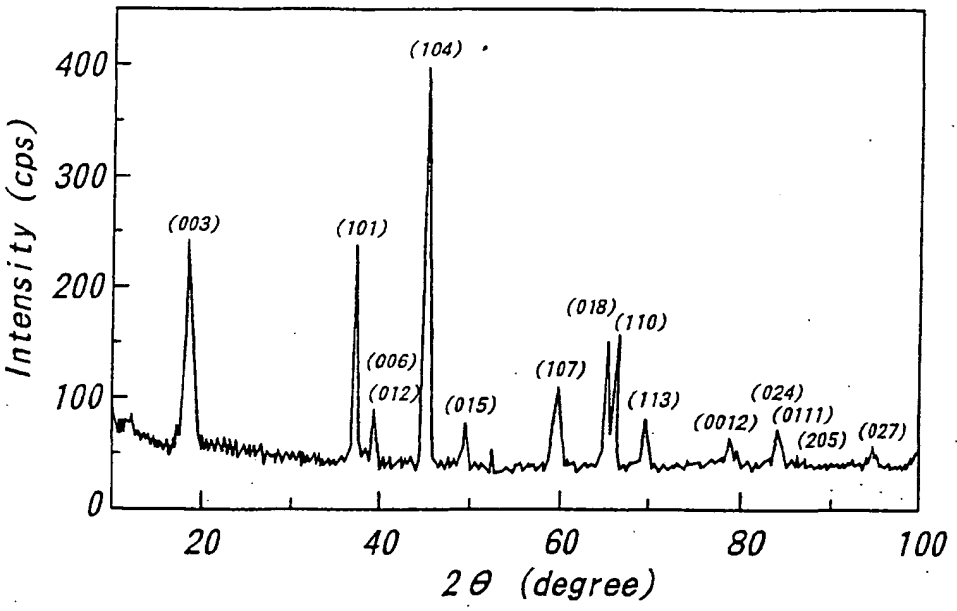
5. A method for forming a thin film as defined in claim 4, wherein the flow rate of the reactive solution is set within 2-200 mL/minute.

6. A method for forming a thin film as defined in claim 4 or 5, further comprising the step of incorporating oxidizer in the reactive solution,
   whereby an oxide thin film including the components of the reactive solution and the anode electrode is formed on the given substrate.

7. A method for forming a thin film as defined in any one of claims 1-6, wherein the reactive solution is composed of a lithium hydroxide water solution and the anode electrode is composed of a cobalt electrode, and thus, a lithium cobalt thin film is formed as the compound thin film.

8. A method for forming a thin film as defined in claim 7, wherein the oxidizer is hydrogen peroxide.

FIG. 1


Intensity (cps)
400
300
200
100
0
20
40
60
80
100
2θ (degree)
(003)
(101)
(104)
(006)
(012)
(015)
(107)
(018)
(110)
(113)
(0012)
(024)
(0111)
(205)
(027)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 10 6731

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	YOSHIMURA M ET AL: "Direct fabrication of thin-film LiNiO2 electrodes in LiOH solution by electrochemical-hydrothermal method" SOLID STATE IONICS,NL,NORTH HOLLAND PUB. COMPANY. AMSTERDAM, vol. 106, no. 1-2, 1 February 1998 (1998-02-01), pages 39-44, XP004108834 ISSN: 0167-2738 * abstract * * page 40, left-hand column, line 1,2 * * page 41, left-hand column, paragraph 2 * ---	1,4	H01M4/04
A	US 3 520 780 A (FINDL EUGENE ET AL) 14 July 1970 (1970-07-14) * column 2, line 22 - line 24 * * column 3, line 25 - line 35 * * column 4, line 3 - line 15 * * claims 1,5 * ---	1-6	
A	US 5 597 661 A (TAKEUCHI MASATAKA ET AL) 28 January 1997 (1997-01-28) * column 12, line 66 - column 13, line 3 * * example 23 * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) H01M C25D C25B
A	EP 0 319 489 A (PERMELEC ELECTRODE LTD) 7 June 1989 (1989-06-07) * column 2, line 28 - line 45 * * column 3, line 34 - line 52 * * column 4, line 26 - line 50 * * examples 1,2,4,8 * * claims 5,14 * -----	1-6	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 June 2001	Métais, S

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document

T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 10 6731

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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14-06-2001

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 49157	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IL 03/00623	International filing date *(day/month/year)* 29/07/2003	(Earliest) Priority Date *(day/month/year)* 17/10/2002
Applicant TEL-AVIV UNIVERSITY FUTURE TECHNOLOGY DEVELOPMENT		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. 1

   [X] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL 03/00623

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

A method for producing a microbattery (100) including providing a conductive substrate(102), forming a thin film cathodic layer (108) on at least one surface of the conductive substrate, subsequently forming a thin film electrolyte layer (110) over the cathodic layer and subsequently forming a thin film anodic layer (112) over the electrolyte layer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL 03/00623

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M10/40 H01M4/04 H01M4/02 H01M4/58 C25D9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 550 015 A (RECH APPLIC ELECTROCHIMIQUE) 1 February 1985 (1985-02-01)	1-3, 7-12,14, 15, 19-24, 26-28, 32-37, 39,40, 44-49
Y	page 2, line 11 - page 3, line 8	4-6,13, 16-18, 25, 29-31, 38, 41-43,50
	claims 9,10	
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 November 2004	29/11/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Standaert, F

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL 03/00623

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 197 450 B1 (PELED EMANUEL ET AL) 6 March 2001 (2001-03-06) cited in the application column 2, line 26 - line 58 column 3, line 29 - line 40 column 4, line 36 - line 39	1-50
Y	EP 0 450 848 A (GOULD INC) 9 October 1991 (1991-10-09) page 2, line 8 - line 13 page 3, line 40 - line 57	4-6,13, 16-18, 25, 29-31, 38, 41-43,50
A	ALBU-YARON A ET AL: "Influence of the electrochemical deposition parameters on the microstructure of MoS2 thin films" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 361-362, no. 1, February 2000 (2000-02), pages 223-228, XP004187475 ISSN: 0040-6090 cited in the application page 223, left-hand column, line 1 - right-hand column, line 21	13,25, 38,50
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IL 03/00623

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